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(54) **RARE EARTH METAL/NICKEL-BASE HYDROGEN ABSORBING ALLOY, PROCESS FOR PREPARING THE SAME, AND NEGATIVE ELECTRODE FOR NICKEL-HYDROGEN SECONDARY BATTERY**

(57) A rare earth metal/nickel-base hydrogen absorbing alloy having a composition represented by formula (1): $(R_{1-x} L_x)(Ni_{1-y} M_y)_z$, (wherein R represents La, Ce, Pr, or Nd; L represents Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc, Mg, or Ca; and M represents Co, Al, Mn, Fe, Cu, Zr, Ti, Mo, Si, V, Cr, Nb, Hf, Ta, W, B, or C; $0.01 \leq x \leq 0.1$; $0 \leq y \leq 0.5$; and $4.5 \leq z \leq 5.0$), wherein the content of crystals with the number of reversed-phase boundaries present perpendicularly to the C axis of crystal grains in the alloy being 2 to less than 20 per 20 nm in the direction of the C axis is 10 to less than 95 vol.% and the amount of L in the formula (1) present in the reversed-phase region is 60 to less than 95 % of the amount of L added. The negative electrode for the nickel-hydrogen secondary battery can simultaneously improve all of the initial activity, battery capacity, and battery life.

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as compared to the conventional rare earth metal-nickel hydrogen storage alloy which can be used as an anode material for a nickel-hydrogen rechargeable battery.

It is another object of the present invention to provide an anode for a nickel-hydrogen rechargeable battery which achieves the high initial activity, the high battery capacity, and the long battery life all at the same time.

The present inventor has reached the present invention by paying the attention to the following points in relation to the facts that an alloy having a composition with decreased content of transition metals mainly containing nickel relative to the rare earth metals (referred to as "R-rich composition" hereinbelow) has larger hydrogen storage capacity than the AB₅ type alloy, but the practical hydrogen-storage capacity thereof is lower than the AB₅ type alloy because a binding force between the alloy and hydrogen in absorbing hydrogen is too strong, which leads to rise in hydrogen desorbing temperature.

First, the present inventor has found that, by generating a particular amount of crystals containing antiphase boundaries therein in a particular distribution in an alloy with R-rich composition, initial activity for hydrogen absorption and desorption is improved, and that presence of such antiphase boundaries favorably affects prevention of decrepitation due to absorption and desorption of hydrogen. It is believed that the presence of such antiphase boundaries favorably affects the hydrogen storage properties because rare earth elements are arranged along the antiphase boundaries, through which hydrogen can easily be transferred.

Second, the introduction of the antiphase boundaries causes disadvantages in the battery life since the antiphase area has high density of rare earth elements, resulting in inferior corrosion resistance against an electrolytic solution. In the light of this disadvantage, the present inventor substituted a portion of the light rare earth elements employed in the A-site by a particular elements including heavy rare earth elements (referred to as "substitution element L" hereinbelow) to arrange a large amount of the substitution element L in the antiphase area, thereby improving the battery life.

Third, the present inventor has found that the alloy having crystals of the LaNi₅ type single-phase structure containing the particular antiphase boundaries as described above can be obtained by supplying an alloy melt of a particular composition onto a roll of a particular surface roughness under particular cooling conditions to cast into an alloy of a particular thickness.

According to the present invention, there is provided a rare earth metal-nickel hydrogen storage alloy (referred to as "hydrogen storage alloy B" hereinbelow) having a composition (referred to as "composition A" hereinbelow) represented by the formula (1)



wherein R stands for La, Ce, Pr, Nd, or mixtures thereof, L stands for Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc, Mg, Ca, or mixtures thereof, M stands for Co, Al, Mn, Fe, Cu, Zr, Ti, Mo, Si, V, Cr, Nb, Hf, Ta, W, B, C, or mixtures thereof, x, y and z satisfy the formulae of $0.01 \leq x \leq 0.1$, $0 \leq y \leq 0.5$, and $4.5 \leq z \leq 5.0$, respectively, crystals in said alloy being of a LaNi₅ type single phase structure, said alloy including in an amount of not less than 10 volume % and less than 95 volume % thereof crystals each containing not less than 2 and less than 20 antiphase boundaries extending perpendicular to C-axis of a crystal grain of the alloy per 20 nm along the C-axis, not less than 60 % and less than 95 % of added amount of said element represented by L in the formula (1) being arranged in antiphase areas.

According to the present invention, there is provided a method for producing the hydrogen storage alloy B comprising the steps of uniformly solidifying an alloy melt having the composition A represented by the formula (1) above to have a thickness of 0.1 to 2.0 mm under cooling conditions wherein a supercooling degree is 50 to 500 °C and a cooling rate is 1000 to 10000 °C/sec. using a roll casting device having a roll with a surface roughness of 30 to 150 μm in ten-point mean roughness (Rz), thereby obtaining an alloy; and heating said alloy in vacuum or an inert atmosphere at 800 to 1000 °C for 0.1 to 12 hours.

According to the present invention, there is further provided an anode for a nickel-hydrogen rechargeable battery containing as an anode material the hydrogen storage alloy B and an electrically conductive material.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photograph taken by a high-resolution transmission electron microscope for determining the number of the antiphase boundaries contained in the crystal grains in an alloy in the form of ribbons prepared in Example 1.

Fig. 2 is a photograph taken by a high-resolution transmission electron microscope for determining the content of the crystal grains containing the antiphase boundaries therein in the alloy in the form of ribbons prepared in Example 1.

BEST MODE FOR CARRYING OUT THE INVENTION

The hydrogen storage alloy B of the present invention is a rare earth metal-nickel hydrogen storage alloy which has the composition A represented by the formula (1) above, in which crystals have a LaNi₅ type single phase structure, which includes in an amount of not less than 10 volume % and less than 95 volume % thereof crystals each containing

more than 0.1, more preferably 0.01 to 0.03 in atomic ratio. Mo has effects of improving the activity, and of accelerating the hydrogen absorption-desorption rate. The mixing ratio of Mo is preferably not more than 0.05, more preferably 0.01 to 0.02 in atomic ratio. Si has an effect of lowering the equilibrium pressure of hydrogen. The mixing ratio of Si is preferably 0.01 to 0.25, more preferably 0.02 to 0.05 in atomic ratio. V has an effect of facilitating formation of the antiphase boundaries. The mixing ratio of V is preferably 0.01 to 0.2, more preferably 0.02 to 0.05 in atomic ratio. Cr has an anti-cracking effect. The mixing ratio of Cr is preferably 0.01 to 0.2, more preferably 0.03 to 0.1 in atomic ratio. Nb has an anti-cracking effect. The mixing ratio of Nb is preferably 0.01 to 0.05, more preferably 0.02 to 0.04 in atomic ratio. Hf has an effect of improving the hysteresis properties. The mixing ratio of Hf is preferably not more than 0.05, more preferably 0.01 to 0.03 in atomic ratio. Ta has an effect of improving the hysteresis properties. The mixing ratio of Ta is preferably 0.01 to 0.05, more preferably 0.02 to 0.03 in atomic ratio. W has effects of improving the activity, and of accelerating the hydrogen absorption-desorption rate. The mixing ratio of W is preferably not more than 0.05, more preferably 0.01 to 0.03 in atomic ratio. B has effects of improving the activity, and of accelerating the hydrogen absorption-desorption rate. The mixing ratio of B is preferably not more than 0.03, more preferably 0.01 to 0.02 in atomic ratio. C has an effect of accelerating the hydrogen absorption-desorption rate. The mixing ratio of C is preferably not more than 0.03, more preferably 0.01 to 0.02 in atomic ratio.

The hydrogen storage alloy B of the present invention may contain impurities which are inevitably contained in each of the starting material of the composition A, or during the manufacturing process of the hydrogen storage alloy B.

Specific examples of the composition A represented by the formula (1) may preferably include the following alloy compositions:

$\text{La}_{0.25}\text{Ce}_{0.49}\text{Pr}_{0.05}\text{Nd}_{0.2}\text{Gd}_{0.02}\text{Ni}_{3.61}\text{Al}_{0.2}\text{Co}_{0.54}\text{Mn}_{0.5}\text{Fe}_{0.02}$,
 $\text{La}_{0.24}\text{Ce}_{0.48}\text{Pr}_{0.05}\text{Nd}_{0.19}\text{Gd}_{0.04}\text{Ni}_{3.51}\text{Al}_{0.2}\text{Co}_{0.53}\text{Mn}_{0.49}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Gd}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Dy}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Er}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Yb}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Y}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Sc}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Mg}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Ca}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Gd}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}\text{Ti}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Gd}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}\text{Zr}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Gd}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}\text{B}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Gd}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}\text{Mo}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Gd}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}\text{W}_{0.02}$,
 $\text{La}_{0.23}\text{Ce}_{0.46}\text{Pr}_{0.05}\text{Nd}_{0.18}\text{Gd}_{0.08}\text{Ni}_{3.38}\text{Al}_{0.19}\text{Co}_{0.5}\text{Mn}_{0.47}\text{Fe}_{0.02}\text{Cu}_{0.02}$.

In the present method for producing the hydrogen storage alloy B, a mixture of the starting metal materials mixed to have the composition A is melted, and the obtained alloy melt is uniformly solidified to have a thickness of 0.1 to 2.0 mm under the cooling conditions wherein the supercooling degree is 50 to 500 °C and the cooling rate is 1000 to 10000 °C/sec., preferably 3000 to 10000 °C/sec. using a roll casting device having a roll with the particular surface roughness.

In this case, the supercooling degree refers to a value of (melting point of the alloy) - (actual temperature of the alloy melt below the melting point). In detail, "supercooling" is a phenomenon wherein an alloy melt is not actually solidified even when it is cooled down to the melting point of the alloy, but when the temperature of the alloy melt is further declined to reach the nucleation temperature, fine solid phases, i.e. crystals are formed in the alloy melt to cause solidification of the alloy melt for the first time. The supercooling degree may be controlled by, for example, controlling the temperature of the alloy melt prepared by using a crucible or the like and suitably adjusting the time and speed for transferring the alloy melt to a single roll for solidification. If the supercooling degree and the cooling rate are outside the above requisite ranges, an alloy having the desired antiphase boundaries precipitated cannot be obtained.

The above mentioned roll casting device has a single roll or double rolls of internally water-cooled type or the like, on the surface of which an alloy melt is cooled and solidified. In the roll casting device, the surface roughness of the roll is defined by the ten-point mean roughness (Rz). In the method of the present invention, the alloy melt is cooled and solidified using a roll having surface roughness of 30 to 150 μm, preferably 60 to 120 μm in the ten-point mean roughness (Rz).

The ten-point mean roughness (Rz) is defined in JIS B0601-1994 (corresponding to ISO 468), and is represented by the sum of the average of absolute values of the heights of the highest to the fifth highest peaks of the roughness curve of the roll surface measured vertically from the mean line, and the average of absolute values of the depths of the deepest to the fifth deepest valleys of the roughness curve of the roll surface. The ten-point mean roughness (Rz) may be measured using a commercially available stylus type digital surface roughness measuring device based on the same

weight of the anode material.

The anode for a nickel-hydrogen rechargeable battery of the present invention may contain a binder in addition to the above requisite components. Preferred examples of the binder may include an ethylene tetrafluoride-propylene hexafluoride copolymer (FEP), polytetrafluoroethylene, carboxymethyl cellulose, or the like. The content of the binder is preferably less than 10 % by weight of the total weight of the anode material.

The anode for a nickel-hydrogen rechargeable battery of the present invention may be prepared, for example, by binding the anode material on a collector body of a conductive material such as nickel mesh, nickel or copper expanded metal, nickel or copper punched metal, foamed nickel, and woolen nickel. The binding may be carried out by a rolling press method, a molding press method, or the like into the form of preferably a sheet or a pellet. The obtained anode can be used in the same way as an anode for an ordinary nickel-hydrogen rechargeable battery to produce a rechargeable battery.

The hydrogen storage alloy B of the present invention can exhibit high initial activity, high electrical capacity, and long battery life all at the same time when it is used for an anode material for a nickel-hydrogen rechargeable battery. According to the present invention, such hydrogen storage alloy B can be obtained in a practical manner. Further, since the anode for a nickel-hydrogen rechargeable battery of the present invention exhibits high initial activity, high electrical capacity, and long battery life at the same time, it is expected to be demanded in place of a conventional anode.

Examples

The present invention will now be explained in more detail with reference to Examples and Comparative Examples, but the present invention is not limited thereto.

Example 1

A starting material was prepared so that the composition thereof was 8.3 parts by weight of La, 16.3 parts by weight of Ce, 1.7 parts by weight of Pr, 6.9 parts by weight of Nd, 0.75 parts by weight of Gd, 50.4 parts by weight of Ni, 1.3 parts by weight of Al, 7.6 parts by weight of Co, 6.5 parts by weight of Mn, and 0.3 parts by weight of Fe, and then melted in an argon atmosphere by a high frequency induction furnace to obtain an alloy melt. The obtained alloy melt was formed into alloy ribbons with the thickness of 0.3 to 0.4 mm under the conditions of the supercooling degree of 150 °C and the cooling rate of 2000 to 5000 °C/sec. using a single roll casting device having a water-cooled copper roll with the surface roughness of 100 μm in the ten-point mean roughness (R_z). The obtained alloy was heated in an argon atmosphere at 950 °C for 4 hours. The results of the calculation of the composition of the obtained alloy into atomic ratio and the values of x, y, and z in the formula (1) are shown in Table 1.

Powders of the obtained alloy were determined of X-ray diffraction pattern by an X-ray diffraction apparatus manufactured by RIGAKU CORPORATION, thereby confirming that the alloy had LaNi_5 type single phase structure. The alloy was observed in the (100) plane of the crystal grain under a high-resolution transmission electron microscope (JEL4000EX) manufactured by JOEL LTD. to determine the number of the antiphase boundaries extending perpendicular to the C-axis of the crystal grain of the alloy per 20 nm along the C-axis, and the content of the crystal grains containing the antiphase boundaries included in the alloy. Further, the amount of Gd present in the antiphase area was determined by high-resolution EDX spectrometry. The results are shown in Table 2. Further, the photograph taken by the microscope used for determining the number of the antiphase boundaries extending perpendicular to the C-axis of the crystal gain per 20 nm is shown in Fig. 1, and the photograph taken by the microscope used for determining the content of the crystal grains containing the antiphase boundaries is shown in Fig. 2. In the photographs, A in Fig. 1 denotes the antiphase area, and B in Fig. 2 denotes the portion corresponding to Fig. 1 before enlargement.

Subsequently, the alloy was measured of the hydrogen storage capacity and the hydrogen storage pressure using an automated Sievert's-type PCT measuring apparatus manufactured by LESCA CO., LTD. according to JIS H7201 (1991) "Method for Measuring Pressure-Composition Diagram (PCT curve) of Hydrogen Storage Alloy". The results are shown in Table 2.

Next, the alloy was coarsely crushed in a stamp mill, and further pulverized by a planetary ball mill in a hexane solvent into powders of the average particle size of 80 μm . 10 g of the obtained alloy powders, 1 g of copper powders as an electrically conductive material, and 0.3 g of FEP powders (ethylene tetrafluoride-propylene hexafluoride copolymer) as a binder were mixed together to produce a pellet electrode with 20 mm diameter. The obtained electrode was immersed in a 6N KOH solution to produce a battery using a mercury oxide reference electrode, and the electrode characteristics were determined with a potentiogalvanostat (manufactured by HOKUTO DENKO CORPORATION). The results are shown in Table 2.

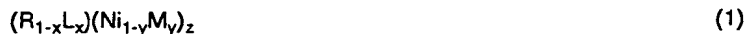
The initial activity and the battery life were measured on the basis of the point where the battery capacity reached the constant level after repeated charging and discharging. The battery life was determined by comparing the capacity at 100 cycles with the capacity at the constant level.

Table 1

	Example *										Comparative Example											
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	1	2	3	4	5	
Alloy Composition (Atomic Ratio)	La	0.25	0.24	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.25	0.20	0.23	0.23	0.23	
	Ce	0.49	0.48	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.50	0.40	0.46	0.46	0.46	
	Pr	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.04	0.05	0.05	0.05	
	Nd	0.20	0.19	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.20	0.16	0.18	0.18	0.18	
	Gd	0.20	0.04	0.08							0.08	0.08	0.08	0.08	0.08	0.08		0.20	0.08	0.08	0.08	
	Dy				0.08																	
	Er					0.08																
	Yb						0.08															
	Y							0.08														
	Sc								0.08													
	Mg									0.08												
	Ca										0.08											
	Ni	3.61	3.51	3.38	3.38	3.33	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38
	Al	0.20	0.20	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
	Co	0.54	0.53	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Mn	0.50	0.49	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	
Fe	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	
Ti											0.02											
Zr												0.02										
B													0.02									
Mo														0.02								
W															0.02							
Cu																0.02						
Value of x	0.02	0.04	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.20	0.08	0.08	0.08	
Value of y	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	
Value of z	4.87	4.75	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	

Claims

1. A rare earth metal-nickel hydrogen storage alloy having a composition represented by the formula (1)



wherein R stands for La, Ce, Pr, Nd, or mixtures thereof, L stands for Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc, Mg, Ca, or mixtures thereof, M stands for Co, Al, Mn, Fe, Cu, Zr, Ti, Mo, Si, V, Cr, Nb, Hf, Ta, W, B, C, or mixtures thereof, x, y and z satisfy the formulae of $0.01 \leq x \leq 0.1$, $0 \leq y \leq 0.5$, and $4.5 \leq z \leq 5.0$, respectively, crystals in said alloy being of a $LaNi_5$ type single phase structure, said alloy including in an amount of not less than 10 volume % and less than 95 volume % thereof crystals each containing not less than 2 and less than 20 antiphase boundaries extending perpendicular to C-axis of a crystal grain of the alloy per 20 nm along the C-axis, not less than 60 % and less than 95 % of added amount of said element represented by L in the formula (1) being arranged in antiphase areas.

2. The rare earth metal-nickel hydrogen storage alloy as claimed in claim 1 wherein x in the formula (1) is within the range of $0.05 \leq x \leq 0.09$.

3. A method for producing the rare earth metal-nickel hydrogen storage alloy as claimed in claim 1 comprising the steps of uniformly solidifying an alloy melt having a composition represented by the formula (1)



wherein R stands for La, Ce, Pr, Nd, or mixtures thereof, L stands for Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc, Mg, Ca, or mixtures thereof, M stands for Co, Al, Mn, Fe, Cu, Zr, Ti, Mo, Si, V, Cr, Nb, Hf, Ta, W, B, C, or mixtures thereof, x, y and z satisfy the formulae of $0.01 \leq x \leq 0.1$, $0 \leq y \leq 0.5$, and $4.5 \leq z \leq 5.0$, respectively, to have a thickness of 0.1 to 2.0 mm under cooling conditions wherein a supercooling degree is 50 to 500 °C and a cooling rate is 1000 to 10000 °C/sec. using a roll casting device having a roll with a surface roughness of 30 to 150 µm in ten-point mean roughness (Rz), thereby obtaining an alloy; and heating said alloy in vacuum or an inert atmosphere at 800 to 1000 °C for 0.1 to 12 hours.

4. The method as claimed in claim 3 wherein said roll has a surface roughness of 60 to 120 µm in ten-point mean roughness (Rz).

5. The method as claimed in claim 3 wherein said heating step is carried out at 850 to 950 °C.

6. An anode for a nickel-hydrogen rechargeable battery containing as an anode material the rare earth metal-nickel hydrogen storage alloy as claimed in claim 1 and an electrically conductive material.

7. The anode for a nickel-hydrogen rechargeable battery as claimed in claim 6 wherein a particle size of said rare earth metal-nickel hydrogen storage alloy is 20 to 100 µm, and a particle size of said electrically conductive material is 1 to 10 µm.

8. The anode for a nickel-hydrogen rechargeable battery as claimed in claim 6 wherein a content of said rare earth metal-nickel hydrogen storage alloy is 70 to 95 % by weight of the total weight of the anode material, and a content of said electrically conductive material is 5 to 20 % by weight of the total weight of the anode material.

9. The anode for a nickel-hydrogen rechargeable battery as claimed in claim 6 wherein said anode material further contain a binder.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/02400

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ C22C19/00, H01M4/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ C22C19/00, H01M4/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1995
Toroku Jitsuyo Shinan Koho	1994 - 1996

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 6-140039, A (Sanyo Electric Co., Ltd.), May 20, 1994 (20. 05. 94) (Family: none)	1 - 9

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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